

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-086186

(43)Date of publication of application : 20.03.2003

(51)Int.Cl. H01M 4/66

H01M 4/02

H01M 4/38

H01M 4/48

H01M 4/58

H01M 10/40

(21)Application number : 2001-272392 (71)Applicant : SONY CORP

(22)Date of filing : 07.09.2001 (72)Inventor : TANIZAKI HIROAKI
KOMARU TOKUO

(54) BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a battery capable of having an excellent cycle characteristic while maintaining a high capacity.

SOLUTION: The battery has in a battery can a rolled electrode body 20 in which a positive electrode 21 and a negative electrode 22 in the form of strips are rolled with a separator 23 placed inbetween. A layer 22b of negative electrode active material contains a single metal element or semimetallic element or its alloy or compound which, together with Li, can form an alloy or compound. A negative-electrode current collector 22a has a tensile strength of not less than 150

N/mm² nor more than 400 N/mm² and has an elongation of not less than 3% nor more than 20% under a tensile test. The negative-electrode current collector 22a expands and contracts as the layer 22b of negative- electrode active material swells and contracts during charge and discharge, preventing separation of the layer 22b. A high capacity can thus be achieved and the cycle life can be extended.

* NOTICES *

**JPO and INPIT are not responsible for any
damages caused by the use of this translation.**

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]A cell provided with an electrolyte with an anode and a negative electrode, comprising:

A negative pole collector whose tensile strength of said negative electrode of more than 150-N/[mm]² is below 400-N/[mm]² and whose elongation by a tensile test is not less than 3% of 20% or less.

A negative electrode active material layer containing at least one sort in a group which consists of a simple substance of a metallic element or metalloid element, an alloy, and a compound which can form a light metal and an alloy.

[Claim 2]The cell according to claim 1 by which said negative pole collector is characterized by Vickers hardness number being 300 or less HV of 100 or more HV.

[Claim 3]The cell according to claim 1, wherein said negative pole collector consists of a metallic foil or alloy foil.

[Claim 4]The cell according to claim 3, wherein said negative pole collector consists of electrolytic foil.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the cell provided with the negative electrode active material layer containing at least one sort in the group which consists of the simple substance of a metallic element or metalloid element, alloy, and compound which can form a light metal and an alloy.

[0002]

[Description of the Prior Art]In recent years, development of the rechargeable battery which has high energy density is demanded with the miniaturization of electronic equipment. There is a lithium secondary battery as a cell which meets this demand. However, a cycle life is short, in order that a lithium metal may carry out dendrite deposition and may inactivate on a negative electrode in a lithium secondary battery at the time of charge.

[0003]Then, the rechargeable lithium-ion battery is developed and produced commercially as what improves this cycle characteristic. In the rechargeable lithium-ion battery, since the graphite material which used the intercalation reaction of lithium (Li) for the negative electrode, or the carbonaceous material adapting occlusion and a secession operation of lithium to the inside of fine pores is used, a lithium metal does not carry out dendrite deposition, but the long cycle life is acquired. Since it is stable in the air, their merit is large also when producing a graphite material and a carbonaceous material industrially.

[0004]However, when a graphite material is used for a negative electrode, the maximum specified by presentation C_6Li of the 1st stage graphite lamellar compound exists in the capacity of a negative electrode. When a carbonaceous material is used for a negative electrode, there is no maximum of capacity like a graphite material, but the specific gravity of a carbonaceous material can fall and controlling minute pore structure cannot raise negative-electrode capacity per unit volume, if it is industrially difficult and fine pores are moreover increased. Although it is known for a certain kind of low-temperature-baking carbonaceous material that the negative-electrode service capacity exceeding 1000 mAh/g is shown, if a cell is constituted by using as an anode the metallic oxide etc. which have big capacity by the electropositive potential beyond 0.8V in an opposite lithium metal, discharge voltage will fall. Since it is such, with the present carbon material, it is thought that it is difficult to deal with long-time-izing of the further hour of use of future electronic equipment or high-energy-density-ization of a power supply. Then, development of the negative electrode active material which was more excellent in occlusion and the capability from which it secedes in lithium is furthered.

[0005]The material to which it applied that a certain kind of lithium metal generated and decomposed reversibly according to electrochemical reaction, for example as negative electrode active material which can on the other hand more realize high capacity is studied. The LiAl alloy is known for many years, and, specifically, the Si alloy is reported to US-Patent Number 4950566.

[0006]

[Problem(s) to be Solved by the Invention]However, there was a problem that negative electrode active material, such as these alloys, had large capacity deterioration, and a charge-and-discharge cycle characteristic got worse easily. When negative electrode active material carries out expansion contraction greatly in connection with charge and discharge, this degradation exfoliates from a charge collector and is considered to originate in it becoming impossible to secure electron conductivity.

[0007]In order to prevent this degradation until now, the negative electrode active material which replaced the part by the element which does not participate in the expansion contraction accompanying the occlusion and secession of lithium is proposed. JP,6-325765,A -- LiSi_aO_b ($0 < a < 2$) is $\text{LiSi}_{1-a}\text{M}_a\text{O}_c$ (M the class metal except the metal or silicon except an alkaline metal) in JP,7-230800,A. [express and] $0 < c$, $0 < d < 1$, and $0 < e < 2$ -- it is -- to JP,7-288130,A, the compound in which a LiAgTe system alloy contains a nonmetallic element and 4B group element except carbon in JP,11-102705,A is indicated. However, even if it uses such negative electrode active material, the characteristic which can still be satisfied is not obtained. Mixing and using carbon for the patent No. 3019402 gazette as negative electrode active material is indicated. However, although this method was effective for the improvement of a cycle life, there was a problem that capacity will fall.

[0008]This invention was made in view of this problem, and the purpose is in providing the cell which can acquire the outstanding cycle characteristic, holding high capacity.

[0009]

[Means for Solving the Problem]A cell by this invention is provided with an electrolyte with an anode and a negative electrode, and a negative electrode, A negative pole collector whose tensile strength of more than 150-N/mm^2 is below 400-N/mm^2 and whose elongation by a tensile test is not less than 3% of 20% or less, It has a negative electrode active material layer containing at least one sort in a group which consists of a simple substance of a metallic element or metalloid element, an alloy, and a compound which can form a light metal and an alloy.

[0010]In a cell by this invention, since tensile strength of a negative pole collector of more than 150-N/mm^2 is below 400-N/mm^2 and elongation by a tensile test is not less than 3% of 20% or less, A negative pole collector expands and contracts corresponding to expansion contraction of a negative electrode active material layer accompanying charge and discharge, and even if it makes it a negative electrode active material layer contain at least one sort in a group which consists of a simple substance of a metallic element or metalloid element, an alloy, and a compound which can form a

light metal and an alloy, exfoliation of a negative electrode active material layer is prevented. Handling also becomes easy and productivity's improves.

[0011]

[Embodiment of the Invention] Hereafter, the 1 embodiment of this invention is described in detail with reference to drawings. Here, it illustrates about the case where lithium (Li) of the light metals is used for an electrode reaction.

[0012] Drawing 1 expresses the section structure of the rechargeable battery concerning the 1 embodiment of this invention. This rechargeable battery is called what is called cylindrical, and has mostly the rolled electrode body 20 by which the band-like anode 21 and the negative electrode 22 were wound around the inside of the hollow cylinder-like battery can 11 via the separator 23. The battery can 11 is constituted by the iron in which plating of nickel (nickel) was carried out, for example, an end part is closed and the other end is opened wide. The electric insulating plates 12 and 13 of the couple are vertically arranged to the winding peripheral surface, respectively so that the inside of the battery can 11 may pinch the rolled electrode body 20.

[0013] The safety valve mechanism 15 provided in the open end part of the battery can 11 inside the battery lid 14 and this battery lid 14 and the feeling-of-heat resistance element (Positive Temperature Coefficient-TC element) 16, the gasket 17 -- passing -- by being closed, it is attached and the inside of the battery can 11 is sealed. The battery lid 14 is constituted by the same material as the battery can 11, for example. It is electrically connected with the battery lid 14 via the feeling-of-heat resistance element 16, and the disc plate 15a is reversed and the safety valve mechanism 15 disconnects the electrical link of the battery lid 14 and the rolled electrode body 20, when the internal pressure of a cell becomes more than fixed with an internal short circuit or heating from the outside. The feeling-of-heat resistance element 16 restricts current according to increase of resistance, if temperature rises, it prevents unusual generation of heat by a high current, and is constituted by barium titanate series semiconductive ceramics. The gasket 17 is constituted by the insulating material, for example, and asphalt is applied to the surface.

[0014] The rolled electrode body 20 is wound focusing on the center pin 24, for example. The positive electrode lead 25 which consists of aluminum (aluminum) etc. is connected to the anode 21 of the rolled electrode body 20, and the negative electrode lead 26 which consists of nickel etc. is connected to the negative electrode 22. By being welded to the safety valve mechanism 15, it is electrically connected with the battery lid 14, and the negative electrode lead 26 is welded to the battery can 11, and the positive electrode lead 25 is electrically connected.

[0015]Drawing 2 expands and expresses a part of rolled electrode body 20 shown in drawing 1. The anode 21 has the structure where the positive active material layer 21b was established in both sides of the positive pole collector 21a which has a field of the couple which counters, for example. Although a graphic display is not carried out, it may be made to establish the positive active material layer 21b only in one side of the positive pole collector 21a. Thickness is 5 micrometers - about 50 micrometers, and the positive pole collector 21a is constituted by metallic foils, such as aluminium foil, nickel foil, or stainless steel foil, for example. Thickness is 20 micrometers, for example, positive active material and if needed, the positive active material layer 21b contains conducting agents, such as carbon black or graphite, and binders, such as polyvinylidene fluoride, and is constituted, for example. The thickness of the positive active material layer 21b is the thickness of the sum total, when the positive active material layer 21b is established in both sides of the positive pole collector 21a.

[0016]As positive active material, a metallic oxide, metallic sulfide, or a specific polymer material is preferred, and any those one sort or two sorts or more are chosen according to the purpose of using a cell, for example.

[0017]As a metallic oxide, the lithium multiple oxide or V_2O_5 which makes Li_xMO_2 a subject is mentioned. Since especially the lithium multiple oxide can make voltage high and can make an energy density high, it is preferred. In the above-mentioned empirical formula, at least one sort of M in the group which consists of one or more kinds of transition metals especially cobalt (Co), nickel, and manganese (Mn) is preferred. The value of x changes with charge-and-discharge states of a cell, and is usually $0.05 \leq x \leq 1.10$. As an example of such a lithium multiple oxide, $LiCoO_2$, $LiNiO_2$, $Li_yNi_{1-y}Co_zO_2$ (y and z change with charge-and-discharge states of a cell, and usually) or it is $0 < y < 1$ and $0.7 < z < 1.02$, $LiMn_2O_4$ etc. which have spinel type structure are mentioned.

[0018]As metallic sulfide, TiS_2 or MoS_2 is mentioned and polyacethylene or polypyrrole is mentioned as a polymer material. $NbSe_2$ other than such positive active material, etc. can be used.

[0019]The negative electrode 22 has the structure where the negative electrode active material layer 22b was established in both sides of the negative pole collector 22a which has a field of the couple which counters like the anode 21. Although a graphic display is not carried out, it may be made to establish the negative electrode active material layer 22b only in one side of the negative pole collector 22a.

[0020]As for the negative pole collector 22a, it is preferred that the tensile strength of more than $150\text{-N}/\text{mm}$ is below $400\text{-N}/\text{mm}$. If it is below $400\text{-N}/\text{mm}$, even if

the negative electrode active material later mentioned at the time of charge will expand, it is because can follow in footsteps of the expansion, it can be extended, and exfoliation of the negative electrode active material layer 22b can be prevented, and the handling at the time of production will become easy if it is more than $150\text{-N}/\text{mm}^2$. Since exfoliation of the negative electrode active material layer 22b can be especially prevented more efficiently if it is below $350\text{-N}/\text{mm}^2$, it is desirable, and if it is more than $180\text{-N}/\text{mm}^2$ and also more than $200\text{-N}/\text{mm}^2$, since the handling at the time of production can be made easier, it is desirable.

[0021]The elongation by the tensile test of the negative pole collector 22a has the preferred not less than 3% ** 8 which is 20% or less. It is because will not be able to follow in footsteps of expansion [the negative electrode active material by charge] if elongation is too small, it will not be able to follow in footsteps of contraction of the negative electrode active material by discharge if too conversely large, but both the negative electrode active material layers 22b will exfoliate and a cycle life will become short. If the elongation of the negative pole collector 22a is not less than 5% or not less than 15%, it is more preferred.

[0022]Tensile strength and elongation use the No. 1 specimen specified to a JISZ2201 metallic-material test piece for tensile test, and are acquired by the metallic material tensile test method specified to JISZ2241. By total elongation method measurement, it computes from the maximum sleeper tension load, and, specifically, let elongation be the elongation after fracture measured till elongation after fracture.

[0023]As for the Vickers hardness number of the negative pole collector 22a, it is preferred that it is [100 or more HV] 300 or less HV. If the negative pole collector 22a goes out easily and it is larger than 300HV on the contrary when winding the time of application-of-pressure molding of the negative electrode active material layer 22b mentioned later, for example or the anode 21, and the negative electrode 22 via the separator 23, if smaller than 100HV, It is because battery capacity will fall as a result of [the] negative electrode active material's expanding and contracting at the time of charge and discharge, the negative electrode active material layer's 22b exfoliating or electric conduction contact nature's not falling. Vickers hardness number is obtained by the Vickers hardness testing method specified to JISZ2244.

[0024]Such a negative pole collector 22a is constituted by alloy foil, such as metallic foils, such as copper (Cu) foil or nickel foil, or copper alloy foil, nickel alloy foil, or stainless steel foil, for example. Electron conductivity has good influence on a heavy loading characteristic highly, and since it is cheap and easily available, such metallic foils or alloy foil are preferred. If such metallic foils or alloy foil are classified

according to a process, they will be divided into rolling foil and electrolytic foil. Rolling foil is produced by rolling to foil form through between rollers, pressurizing the metal or the alloy mass which is a raw material with a rolling roller for example. Electrolytic foil uses as the negative pole the roller which immersed the lower part into the electrolytic bath, energizes current by making the insoluble anode into a counter electrode, and it is produced by plating metal continuously on the surface of a roller, and stripping off depositing metal continuously from a roller surface, supplying an electrolysis solution from the electrolysis solution supply slit of the anode.

[0025]As the negative pole collector 22a, electrolytic foil is preferred. Electrolytic foil is because elongation is generally 4%, so elongation can be easily adjusted to a mentioned range. On the other hand, since elongation is generally 2%, the rolling foil needs to adjust elongation for heat treatment or chemical softening processing to a mentioned range by *****. As long as these softening processing is before charging a cell, it may be good at any time, for example, after it applies the negative electrode active material layer 22b to the negative pole collector 22a, it may be performed, and it may be performed after a cell assembly.

[0026]It is preferred that it is not less than 8 micrometers, for example, and if the thickness of the negative pole collector 22a is not less than 10 micrometers, it is more preferred. Capacity becomes high so that it is thin, but it is because the handling at the time of production becomes difficult and the heavy loading characteristic of a cell will get worse by the increase in current collection resistance, if too thin. It is preferred again that it is 30 micrometers or less for example, and if the thickness of the negative pole collector 22a is 20 micrometers or less, it is more preferred. If thick, the handling at the time of production will be easy, and current collection resistance will also resist, but it is because capacity will fall if too thick.

[0027]The negative electrode active material layer 22b is constituted including binders, such as polyvinylidene fluoride, negative electrode active material and if needed. It is preferred that the simple substance of a metallic element or metalloid element, alloy, or compound which can form lithium and an alloy is mentioned as negative electrode active material, and at least one of sorts of these is included. It is because high capacity can be obtained. what becomes an alloy from two or more sorts of metallic elements -- in addition, what consists of one or more sorts of metallic elements and one or more sorts of metalloid element is included. There are some with which two of a solid solution, a eutectic crystal (eutectic mixture), an intermetallic compound, or sorts or more of they coexist in the organization.

[0028]As the metallic element which can form lithium and an alloy, or metalloid

element, For example, magnesium (Mg), boron (B), arsenic (As), aluminum, gallium (Ga), Indium (In), silicon (Si), germanium (germanium), tin (Sn), lead (Pb), antimony (Sb), bismuth (Bi), cadmium (Cd), silver (Ag), zinc (Zn), hafnium (Hf), a zirconium (Zr), and yttrium (Y) are mentioned.

[0029]As these alloys or a compound, what is expressed with chemical formula $Ma_sMb_tLi_u$ or chemical formula $Ma_pMc_qMd_r$ is mentioned, for example. In these chemical formulas, Ma expresses at least one sort in the metallic element and metalloid element which can form lithium and an alloy, Mb expresses at least one sort in metallic elements other than lithium and Ma, and metalloid element, Mc expresses at least one sort of a nonmetallic element, and Md expresses at least one sort in metallic elements other than Ma, and metalloid element matter. The values of s, t, u, p, q, and r are $s > 0$, $t \geq 0$, $u \geq 0$, $p > 0$, $q \geq 0$, and $r \geq 0$, respectively.

[0030]As negative electrode active material, silicon, tin, these alloys, or a compound has desirable especially preferred especially simple substance of 4B fellows' metallic element, or metalloid element, alloy, or compound. It is because higher capacity can be obtained. The alloy or compound containing at least one sort in the 2nd element group that consists of metallic elements, metalloid elements, and nonmetallic elements other than at least one sort in the 1st element group that consists of the metallic element and metalloid element which can form lithium and an alloy, and this 1st element is also preferred. It is because the outstanding cycle characteristic can be acquired. As for these, the thing of a crystalline substance may also be amorphous.

[0031]If an example is concretely given about such an alloy or a compound, SiB_4 , SiB_6 , Mg_2Si , Mg_2Sn , $nickel_2Si$, $TiSi_2$, $MoSi_2$, $CoSi_2$, $NiSi_2$, $CaSi_2$, $CrSi_2$, Cu_5Si , Chemical formula $MiMh_j$, such as $FeSi_2$, $MnSi_2$, $NbSi_2$, $TaSi_2$, VSi_2 , WSi_2 , or $ZnSi_2$ (Mi silicon or tin) [express and] Mh expresses one or more sorts of metallic elements -- $j \geq 0$ -- it is -- the alloy or compound expressed. Or there is SiC , Si_3N_4 , Si_2N_2O , $germanium_2N_2O$, SiO , ($0 < V \leq 2$), SnO_w ($0 < W \leq 2$), $LiSiO$, or $LiSnO$.

[0032]As other alloys or compounds, a LiAl alloy, a LiAlMe alloy (Me expresses at least one sort in the group which consists of 2A group element, 3B group element, a 4B group element, and a transition metal element), an AISb alloy, or a CuMgSb alloy is mentioned, for example.

[0033]Such an alloy or a compound is obtained by the mechanical alloying method or the method of mixing a raw material and heat-treating under an inert atmosphere or a reducing atmosphere, for example.

[0034]The negative electrode active material layer 22b may be added to the simple substance of a metallic element or metalloid element, alloy, or compound which can

form lithium and an alloy again, and may contain other negative electrode active material. As other negative electrode active material, occlusion and the carbon material which can be broken away, a metallic oxide, or a polymer material is mentioned in lithium. As a carbon material, nongraphitizing carbon, graphitizing carbon, black lead, carbon black, fibrous carbon, or pyrolysis nature carbon is mentioned, for example. The tin oxide (SnO_2) etc. are mentioned as a metallic oxide, and polyacetylene or polypyrrole is mentioned as a polymer material.

[0035]The thickness of the negative electrode active material layer 22b is 200 micrometers, for example. This thickness is the thickness of that sum total, when the negative electrode active material layer 22b is established in both sides of the negative pole collector 22a.

[0036]The separator 23 is constituted by the porous membrane which consists of inorganic materials, such as a porous membrane which consists of material of the polyolefin system of polypropylene or polyethylene, for example, or a nonwoven fabric made from ceramics, and may be made into the structure which laminated these two or more sorts of porous membranes.

[0037]The electrolysis solution which is a liquefied electrolyte is impregnated with this separator 23. This electrolysis solution is constituted including a solvent and lithium salt which is the electrolyte salt dissolved in this solvent, for example. A solvent makes electrolyte salt dissociate. As a solvent, for example Propylene carbonate, ethylene carbonate, Diethyl carbonate, dimethyl carbonate, 1, 2-dimethoxyethane, 1,2-diethoxyethane, gamma-butyrolactone, a tetrahydrofuran, 2-methyltetrahydrofuran, 1,3-dioxolane, 4-methyl-1,3-dioxolane, Diethylether, sulfolane, methyl sulfolane, acetonitrile, propionitrile, an anisole, acetate ester, butylate, propionate ester, etc. are mentioned, and 1 of any sorts of these and two sorts or more are mixed, and are used.

[0038]As lithium salt, LiClO_4 , LiAsF_6 , LiPF_6 , LiBF_4 , $\text{Li}(\text{C}_6\text{H}_5)_4$, LiCH_3SO_3 , LiCF_3SO_3 , LiCl , LiBr , etc. are mentioned, 1 of any sorts of these and two sorts or more are mixed, and are used.

[0039]This rechargeable battery can be manufactured as follows, for example.

[0040]First, for example, occlusion, the positive active material which can be broken away, a conducting agent, and a binder are mixed for lithium, positive electrode mixture is prepared, this positive electrode mixture is distributed to solvents, such as N-methyl-2-pyrrolidone, and it is considered as a paste state positive electrode mixture slurry. After applying this positive electrode mixture slurry to the positive pole collector 21a and drying a solvent, compression molding is carried out with a roller press machine etc., the positive active material layer 21b is formed, and the anode 21 is

produced.

[0041]Subsequently, for example, occlusion, the negative electrode active material which can be broken away, and a binder are mixed for lithium, negative electrode mixture is prepared, this negative electrode mixture is distributed to solvents, such as N-methyl-2-pyrrolidone, and it is considered as a paste state negative electrode mixture slurry. After applying this negative electrode mixture slurry to the negative pole collector 22a and drying a solvent, compression molding is carried out with a roller press machine etc., the negative electrode active material layer 22b is formed, and the negative electrode 22 is produced.

[0042]Then, the positive electrode lead 25 is attached to the positive pole collector 21a by welding etc., and the negative electrode lead 26 is attached to the negative pole collector 22a by welding etc. After it, weld the tip part of winding and the positive electrode lead 25 to the safety valve mechanism 15 via the separator 23, and the anode 21 and the negative electrode 22. The tip part of the negative electrode lead 26 is welded to the battery can 11, and is stored inside the battery can 11 on both sides of the anode 21 and the negative electrode 22 which were wound with the electric insulating plates 12 and 13 of a couple. After storing the anode 21 and the negative electrode 22 inside the battery can 11, an electrolysis solution is injected into the inside of the battery can 11, and it impregnates with the separator 23. the open end of after it and the battery can 11 -- the battery lid 14, the safety valve mechanism 15, and the feeling-of-heat resistance element 16 -- the gasket 17 -- passing -- it fixes by closing. Thereby, the rechargeable battery shown in drawing 1 is formed.

[0043]This rechargeable battery acts as follows.

[0044]In this rechargeable battery, if it charges, a lithium ion will secede from the anode 21 and occlusion will be carried out to the negative electrode 22 via the electrolysis solution impregnated with the separator 23, for example. If it discharges, a lithium ion will secede from the negative electrode 22, and occlusion will be carried out to the anode 21 via the electrolysis solution impregnated with the separator 23, for example. Since the tensile strength of the negative pole collector 22a of more than 150-N/mm^2 is below 400-N/mm^2 and the elongation by a tensile test is not less than 3% of 20% or less here, The negative pole collector 22a expands and contracts corresponding to expansion contraction of the negative electrode active material layer 22b accompanying charge and discharge, and exfoliation of the negative electrode active material layer 22b is prevented. Handling also becomes easy and productivity's improves.

[0045]Thus, since it was made to make elongation according [more than 150-N/mm^2 / 2] the tensile strength of the negative pole collector 22a to below 400-N/mm^2 and a

tensile test into 20% or less not less than 3% according to this embodiment, The negative pole collector 22a can be expanded and contracted corresponding to expansion contraction of the negative electrode active material layer 22b. Therefore, even if the negative electrode active material layer 22b contains at least one sort in the group which consists of the simple substance of a metallic element or metalloid element, alloy, and compound which can form material with large expansion contraction, for example, lithium and an alloy, exfoliation of the negative electrode active material layer 22b can be prevented. Therefore, high capacity can be obtained and a cycle life can be lengthened.

[0046]

[Example]The concrete example of this invention is described in detail.

[0047]As Examples 1-7, the rechargeable battery shown in drawing 1 and drawing 2 and the same cylindrical rechargeable battery were produced as follows. Here, with reference to drawing 1 and drawing 2, it explains using the same numerals.

[0048]First, lithium carbonate (Li_2CO_3) and cobalt carbonate (CoCO_3), It mixed at a rate of $\text{Li}_2\text{CO}_3:\text{CoCO}_3=0.5:1$ (mole ratio), it calcinated at 900 °C in the air for 5 hours, and the lithium cobalt multiple oxide (LiCoO_2) which is positive active material was obtained. Subsequently, this lithium cobalt multiple oxide 91 mass part, graphite 6 mass part which is conducting agents, and polyvinylidene fluoride 3 mass part which is binders were mixed, and positive electrode mixture was adjusted. Then, make the N-methyl-2-pyrrolidone which is a solvent distribute this positive electrode mixture, and it is considered as a positive electrode mixture slurry. After applying to both sides of the positive pole collector 21a which consists of 20-micrometer-thick band-like aluminium foil uniformly, having dried them, carrying out compression molding and forming the positive active material layer 21b, it cut in the shape of [55 mm-wide] a strip of paper, and the anode 21 was produced. The positive electrode lead 25 made from aluminum was attached to the end of the positive pole collector 21a after it.

[0049]The silicon powder 20g and the copper powder 80g were mixed, and this mixture was put into the quartz boat, after heating at 1000 °C in argon gas atmosphere, it cooled radiationally to the room temperature, and the lump of the CuSi alloy which is negative electrode active material was obtained. Subsequently, the ball mill ground the lump of the CuSi alloy which was able to get in argon gas atmosphere, and it was presupposed that it is powdered. When this powder was observed with the scanning electron microscope (Scanning Electron Microscope; SEM), that mean particle diameter was about 10 micrometers.

[0050]Then, this CuSi alloy 80 mass part, and scaly graphite 10 mass part and acetylene

black 2 mass part which are negative electrode active material and a conducting agent, After mixing polyvinylidene fluoride 8 mass part which is a binder and adjusting negative electrode mixture, the N-methyl-2-pyrrolidone which is a solvent was made to distribute this negative electrode mixture, and it was considered as the negative electrode mixture slurry. 10-micrometer-thick band-like electrolytic copper foil or beryllium copper foil was prepared as the negative pole collector 22a after it. In that case, in Examples 1-7, as shown in Table 1, the kind of foil is changed, and about Examples 2-7, it heat-treated on the conditions shown in Table 1 in the vacuum, and tensile strength and elongation were changed. Subsequently, after applying a negative electrode mixture slurry to both sides of the negative pole collector 22a uniformly, having dried them, carrying out compression molding and forming the negative electrode active material layer 22b, it cut in the shape of [56 mm-wide] a strip of paper, and the negative electrode 22 was produced. The negative electrode lead 26 made from nickel was attached to the end of the negative pole collector 22a after it.

[0051]

[Table 1]

[0052]After producing the anode 21 and the negative electrode 22, respectively, the

separator 23 which consists of a 25-micrometer-thick fine porosity polyethylene film is prepared, It laminated in order of the negative electrode 22, the separator 23, the anode 21, and the separator 23, this layered product was spirally fixed with winding and adhesive tape many times, and the rolled electrode body 20 with an outer diameter of 18 mm was produced.

[0053]After producing the rolled electrode body 20, pinched the rolled electrode body 20 with the electric insulating plates 12 and 13 of the couple, and the negative electrode lead 26 was welded to the battery can 11, and the positive electrode lead 25 was welded to the safety valve mechanism 15, and it stored inside the iron battery cans 11 which carried out nickel plating of the rolled electrode body 20. The electrolysis solution was injected into the inside of the battery can 11 with the decompression method after it. What dissolved LiPF_6 in the solvent which mixed ethylene carbonate 50 volume % and dimethyl carbonate 50 volume % by the concentration of 1.5 mol/dm^3 was used for the electrolysis solution.

[0054]After injecting an electrolysis solution into the inside of the battery can 11, a cylindrical rechargeable battery 18 mm in diameter and 65 mm in height was obtained about Examples 1-7 by closing the battery lid 14 to the battery can 11 via the gasket 17 which applied asphalt to the surface.

[0055]After dissolving and stripping the negative electrode active material layer 22b from the negative pole collector 22a about some rechargeable batteries concerning acquired Examples 1-7, measurement of tensile strength and elongation was performed by the method explained by the embodiment using Shimadzu autograph AGS-50B. As a specimen, the 56-mm-wide negative electrode 22 was used as it was.

[0056]Charge and discharge were performed under the environment of 20 °C using the rechargeable battery concerning Examples 1-7, and it asked for the service capacity maintenance factor. Charge was performed until the total of charging time reached in the constant voltage of 4.2V in 4 hours, after carrying out at that time until cell voltage amounted to 4.2V in the constant current of 1A, and discharge was performed until cell voltage amounted to 2.5V in the constant current of 1A. The service capacity maintenance factor was computed as the ratio of the service capacity of the 100 cycle eye to the service capacity of 1 cycle eye, i.e. (service capacity of the service capacity / 1 cycle eye of a 100 cycle eye), $\times 100$. The obtained result is shown in Table 1. All of the service capacity of 1 cycle eye were almost the same.

[0057]The defective fraction was investigated using the rechargeable battery concerning Examples 1-7. At that time, when the difference of the open-circuit voltage immediately after initial charge and the open-circuit voltage after neglecting it after initial charge for

24 hours was more than 0.1V, it assumed that the internal short circuit has happened and it was judged that it was poor. The measurement size made each example 100 pieces, and it asked for the percentage of the defective number to 100 pieces.

[0058]As the comparative examples 1-5 over this example, rolled copper foil, beryllium copper foil, or copper tin alloy foil was prepared as the negative pole collector 22a, and others produced the rechargeable battery like this example except for having changed the kind, cooking temperature, and cooking time of foil, as shown in Table 1. It asked for tensile strength, elongation, the service capacity maintenance factor, and the defective fraction about the rechargeable battery of the comparative examples 1-5 as well as this example. It is shown doubling those results with Table 1. Each service capacity of 1 cycle eye was almost the same at the comparative examples 1-5.

[0059]As shown in Table 1, in this example [tensile strength / 2 / below / 400N/mm / elongation] using not less than 3% of negative pole collector 22a, the value with a as high service capacity maintenance factor as not less than 60% was obtained. On the other hand, in the comparative example 2 less than 3% of whose comparative examples 1 and 3 and tensile strength are [elongation] larger than 400-N/mm] 2 , the service capacity maintenance factor was able to obtain only less than 60% and a low value. That is, it turned out that tensile strength can lengthen a cycle life below by 400-N/mm] 2 if elongation uses not less than 3% of negative pole collector 22a.

[0060]In this example [tensile strength] using the negative pole collector 22a more than 150-N/mm] 2 , only the value with tensile strength as high in the comparative examples 4 and 5 using the negative pole collector of less than 150-N/mm] 2 as not less than 10% was obtained to the value with a as low defective fraction as less than 10% having been obtained. That is, when tensile strength used the negative pole collector 22a more than 150-N/mm] 2 , it turned out that the outstanding productivity can be obtained.

[0061]When elongation became large, the tendency for a service capacity maintenance factor to worsen was seen and elongation was made into 20% or less from the result of Examples 1-7, it turned out that a service capacity maintenance factor can be made high with not less than 60%.

[0062]Especially, in Examples 1-4, the result that the service capacity maintenance factor excelled with 70% was obtained, and the result that the defective fraction excelled further with 5% or less was obtained in Examples 1-3. That is, it turned out that a cycle characteristic is more improvable if tensile strength is made below into 350-N/mm] 2 and more than 180-N/mm] 2 makes elongation into 15% or less not less than 5%, and a defective fraction can be reduced if tensile strength is made more than

200-N[mm]².

[0063]As mentioned above, although the embodiment and the example were given and this invention was explained, this invention is not limited to the above-mentioned embodiment and an example, and is variously deformable. For example, although the above-mentioned embodiment and the example gave and explained the example concretely about the material and the manufacturing method of a metallic foil or alloy foil which constitute the negative pole collector 22a, The metallic foil or alloy foil which consists of other materials may be used for the negative pole collector 22a, and the metallic foil or alloy foil obtained by other manufacturing methods may be used.

[0064]Although the above-mentioned embodiment and the example explained the case where the electrolysis solution which is a liquefied electrolyte was used for a solvent, it replaces with an electrolysis solution and may be made to use other electrolytes. As other electrolytes, the thing which mixed the gel electrolyte which made the electrolysis solution hold to a high molecular compound, the solid electrolyte which has ion conductivity, the solid electrolyte, and the electrolysis solution, or the thing which mixed the solid electrolyte and the gel electrolyte is mentioned, for example.

[0065]If an electrolysis solution is absorbed and gelled to a gel electrolyte, various high molecular compounds can be used. As such a high molecular compound, for example Fluorine system high molecular compounds, such as a copolymer of polyvinylidene fluoro RAIDO or vinylidene fluoride, and hexafluoropropylene, Ether system high molecular compounds, such as a bridging body containing polyethylene oxide or polyethylene oxide, or polyacrylonitrile is mentioned. In particular, from a point of oxidation reduction stability, a fluorine system high molecular compound is desirable.

[0066]The inorganic solid electrolyte which consists of the organic solid electrolyte which, for example, made the high molecular compound which has ion conductivity distribute electrolyte salt, ion conducting glass, or an ionicity crystal can be used for a solid electrolyte. Ether system high molecular compounds, such as a bridging body which contains polyethylene oxide or polyethylene oxide as a high molecular compound, for example at this time, ester system high molecular compounds, such as polymethacrylate, and an acrylate system high molecular compound, or into a molecule, it can mix, or copolymerization can be carried out and it can use. Lithium nitride or lithium iodide can be used as an inorganic solid electrolyte.

[0067]Although the cylindrical rechargeable battery which has winding structure was explained in the above-mentioned embodiment and the example, This invention is applicable to the rechargeable battery which has the structure which folded up the

rechargeable battery or anode, and negative electrode of the elliptic type which has winding structure, or the polygon type, or was accumulated similarly. In addition, it is applicable also to rechargeable batteries, such as what is called a coin type, a button type, or a card shape. It is applicable not only to a rechargeable battery but a primary battery.

[0068]In addition, although the above-mentioned embodiment and the example explained the case where lithium was used for an electrode reaction, Alkaline-earth metals, such as other alkaline metals, such as sodium (Na) or potassium (K), magnesium, or calcium (Ca), Or also about the case where other light metal, lithium, or these alloys, such as aluminum, are used, this invention can be applied and the same effect can be acquired. In that case, it replaces with the simple substance of a metallic element or metalloid element, alloy, or compound which can form lithium and an alloy in negative electrode active material, The simple substance of a metallic element or metalloid element, alloy, or compound which can form the light metal and alloy is used, and the substance according to the light metal is used also about positive active material and electrolyte salt. Others can be constituted like the above-mentioned embodiment.

[0069]

[Effect of the Invention]As explained above, according to the cell according to any one of claims 1 to 4. Since it was made to make elongation according [more than 150N/mm^2] the tensile strength of a negative pole collector to below 400N/mm^2 and a tensile test into 20% or less not less than 3%, a negative pole collector can be expanded and contracted corresponding to expansion contraction of the negative electrode active material accompanying charge and discharge. Therefore, even if it uses the simple substance of a metallic element or metalloid element, alloy, or compound which can form material with large expansion contraction, for example, lithium and an alloy, as negative electrode active material, exfoliation of negative electrode active material can be prevented. Therefore, high capacity can be obtained and a cycle life can be lengthened. Handling can also become easy and can raise productivity.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a sectional view showing the composition of the rechargeable battery concerning the 1 embodiment of this invention.

[Drawing 2]It is a sectional view which expands and expresses a part of rolled electrode body in the rechargeable battery shown in drawing 1.

[Description of Notations]

11 [-- Safety valve mechanism,] -- A battery can, 12, 13 -- An electric insulating plate, 14 -- A battery lid, 15 16 [-- An anode, 21a / -- A positive pole collector, 21b / -- A positive active material layer, 22 / -- A negative electrode, 22a / -- A negative pole collector, 22b / -- A negative electrode active material layer, 23 / -- A separator, 24 / -- A center pin, 25 / -- A positive electrode lead, 26 / -- Negative electrode lead] -- A feeling-of-heat resistance element, 17 -- A gasket, 20 -- A rolled electrode body, 21